

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
APPLICATION FOR UNITED STATES LETTERS PATENT**

METAL LOADED CARBON FILAMENTS

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TITLE

METAL LOADED CARBON FILAMENTS

CROSS-REFERENCE TO RELATED APPLICATIONS

Not applicable.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

REFERENCE TO A MICROFICHE APPENDIX

Not applicable.

FIELD OF THE INVENTION

[0001] This invention generally relates to the production of carbon filaments. More specifically, the invention relates to metal loaded carbon filaments and a process for making the same.

BACKGROUND OF THE INVENTION

[0002] Natural gas reserves have been found in remote areas where it is uneconomical to develop the reserves due to the lack of local markets for the gas and the high cost of transporting the gas to distant markets. This high cost is often related to the extremely low temperatures needed to liquefy the highly volatile gas during transport. An alternative is to locally convert the natural gas to products that can be transported more cost effectively.

[0003] Natural gas comprises several components, including alkanes, i.e., saturated hydrocarbons (compounds containing hydrogen [H] and carbon [C]) whose molecules contain carbon atoms linked together by single bonds. The simplest alkanes are methane (CH₄), ethane (CH₃CH₃), and propane (CH₃CH₂CH₃). Exemplary products that natural gas can be used to produce are carbon filaments, which are typically less than about 50 nanometers (nm) in size. One process for forming carbon filaments involves converting alkanes in natural gas to products such as

alkenes (also known as olefins) or carbon monoxide (CO), followed by converting the alkenes and/or the CO to carbon filaments. Alkenes are unsaturated hydrocarbons whose molecules contain one or more pairs of carbon atoms linked together by a double bond. Generally, alkenes are commonly represented by the chemical formula $\text{CH}_2=\text{CHR}$, where C is a carbon atom, H is a hydrogen atom, and R is an atom or pendant molecular group of varying composition. In the ODH process, alkanes are dehydrogenated in the presence of oxygen (O_2) and an ODH catalyst to form alkenes, CO, and H_2 . The alkenes and/or the CO are then thermally decomposed in the presence of a metal catalyst to form carbon filaments. Producing carbon filaments in this manner depends upon an upstream alkenes-generating process to supply the feed components for carbon filament growth.

[0004] In contrast, another process for producing carbon filaments involves converting alkanes in natural gas directly to carbon filaments and thus avoids the costs associated with the intermediate step of converting alkanes to alkenes and CO. The direct conversion of alkanes to carbon filaments is also performed using a metal catalyst.

[0005] Carbon filaments are known for their outstanding mechanical properties such as having relatively high surface areas, aspect ratios, and mechanical strength. Thus, researchers have found useful applications for carbon filaments. For example, they are commonly combined within a polymer matrix to form an engineered composite material. However, the current number of applications of conventional carbon filaments is limited. Therefore, a need exists to develop carbon filaments with properties that allow them to be used for a wide variety of new applications, such as conductive materials or gas storage which are better served by metal-containing carbon filaments.

SUMMARY OF THE INVENTION

[0006] According to an embodiment, a process for producing metal loaded carbon filaments includes forming metal on carbon filaments produced from at least one carbon-containing feed. The carbon-containing feed may comprise an alkane, an alkene, carbon monoxide (CO), or carbon dioxide (CO₂). The metal may be formed on surfaces of previously formed carbon filaments by, for example, electroplating, impregnation, or chemical vapor deposition. Alternatively, the carbon filaments and the metal may be formed concurrently, resulting in the metal being incorporated in the carbon filaments.

[0007] In another embodiment, a carbon-based structure comprises a carbon filament and metal positioned on the carbon filament. In particular, the metal may be incorporated in the carbon filament, or alternatively, it may be positioned on an outside surface of the carbon filament. The carbon-based structure is capable of storing hydrogen and/or natural gas. In yet another embodiment, an article of manufacture includes a carbon filament having metal disposed thereon. The article of manufacture may be, for example, a catalyst or an electrical element.

DESCRIPTION OF DRAWINGS

[0008] The invention, together with further advantages thereof, may best be understood by reference to the following description taken in conjunction with the accompanying drawings in which:

[0009] FIG. 1 is a process flow diagram of an embodiment, wherein hydrocarbons found in natural gas are converted to carbon filaments, followed by forming metal on the carbon filaments.

[0010] FIG. 2 is a process flow diagram of an alternative embodiment to the embodiment shown in FIG. 1.

[0011] FIG. 3 is a process flow diagram of an embodiment, wherein alkenes produced by oxidative dehydrogenation of hydrocarbons are converted to carbon filaments, followed by forming metal on the carbon filaments.

[0012] FIG. 4 is a process flow diagram of an alternative embodiment to the embodiment shown in FIG. 3.

[0013] FIG. 5 depicts a SEM picture of pretreated carbon filaments before metal modification.

[0014] FIG. 6 depicts a SEM picture of carbon filaments coated with lithium oxide by impregnation.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] In the embodiments shown in Figs. 1-4, carbon filaments produced from hydrocarbons are loaded with metal for use in various applications. Fig. 1 depicts an embodiment in which the carbon filaments are produced from alkanes recovered from a gas plant, followed by loading metal on the carbon filaments in a separate reactor. In an alternative embodiment to those shown in Figs. 1 and 2, natural gas is fed directly to CF reactor 16 or CVD/CF reactor 30, respectively, without first being processed in a gas plant 12. Referring to Fig. 1, the carbon filaments are first produced by feeding a natural gas stream 10 comprising alkanes to a gas plant 12. Gas plant 12 includes a separator, e.g., a hydrocarbon splitter for processing feed stream 10 into at least a methane fraction and one or more additional fractions comprising ethane, propane, and butanes and heavier hydrocarbons. Typically, feed stream 14 comprising a mixture of one or more of ethane, propane, and butanes and heavier hydrocarbons is passed from gas plant 12 to a carbon filament (CF) reactor 16, and the methane fraction is fed to another process, for example a synthesis gas production process not shown.

[0016] Within CF reactor 16, feed stream 14 contacts a CF catalyst, i.e., any suitable catalyst for producing carbon filaments from alkanes. As a result, the alkanes present in feed stream 14

decompose, thereby forming carbon filaments that may be, for example, less than about 50 nm in diameter. Reaction products produced in CF reactor 16 comprise carbon filaments, H₂, and unconverted hydrocarbons. The H₂ produced in CF reactor 16 may be recovered using any known separation technique such as membrane separation. Carbon filaments are removed from CF reactor 16 via product stream 18, and H₂ is removed from CF reactor 16 via by-product stream 20. Although not shown, by-product stream 20 can be passed to processes that require H₂, e.g., a Fischer-Tropsch process, a hydrotreater, and a hydrocracker. The unconverted hydrocarbons recovered from CF reactor 16 may be further processed via a recycle stream (not shown) to the CF reactor.

[0017] A nitrogen (N₂) stream 13 and/or a H₂ stream 15 may optionally be fed to CF reactor 16 to improve the heat distribution and contact between the hydrocarbon gases and the CF catalyst, and also to improve certain properties of the carbon filament product. In this embodiment, the molar ratio of carbon to H₂ (C:H₂) being fed to CF reactor 16 preferably ranges from about 1:5 to about 1:0.1, more preferably from about 1:3 to about 1:0.3 and most preferably from about 1:1 to about 1:0.5. The molar ratio of carbon to N₂ (C:N₂) being fed to CF reactor 16 preferably ranges from about 1:2 to about 1:0.1, more preferably from about 1:1 to about 1:0.2, and most preferably from about 1:0.5 to about 1:0.3.

[0018] The CF catalyst contained within CF reactor 16 may be a metal catalyst, which is defined herein as comprising elemental iron, nickel, cobalt, copper, or chromium; alloys comprising the foregoing metals; oxides of the foregoing metals and alloys; and combinations of the foregoing metals, alloys, and oxides. The CF catalyst may be optimized to convert alkanes such as ethane and propane into carbon filaments. Examples of catalysts that may be employed in CF reactor 16 are metals such as nickel and cobalt and commercially available alloys such as MONEL alloy 400 (Ni-Cu) and NICHROME alloy (Ni-Cr). The CF catalyst may take the form of any

appropriate structure such as a wire, disk, gauze, mesh, sheet, sphere, rod, or inert support coated with metal. Further, the CF catalyst may be arranged in a fixed bed, or it may form a fluidized bed within CF reactor 16.

[0019] The CF reactor 16 is configured to support the particular CF catalyst being used and thus may be a fixed bed reactor or a fluidized bed reactor. It is also configured to accommodate harvesting of the carbon filaments upon completion of their growth cycle and to provide for the removal of the carbon filaments from the reactor vessel. The CF reactor 16 may be a continuous reactor, allowing the CF process to operate continuously, or alternatively it may be a batch reactor. A suitable continuous reactor is shown in Fig. 6 of Tibbetts, Vapor Grown Carbon Fibers, NATO ASI Series E: Applied Sciences, Vol. 177, pp. 78 (1989), which is incorporated by reference herein in its entirety.

[0020] Within CF reactor 16, the alkanes are contacted with the CF catalyst in a reaction zone that is maintained at conversion-promoting conditions effective to produce carbon filaments. Preferably, conversion-promoting conditions are the optimum flowrate, gas preheat and/or catalyst temperature. Depending on the catalyst arrangement, preheating feed stream 14 may be preferred over preheating the catalyst. The temperature of the gases contacting the catalyst preferably ranges from about 350°C to about 1000°C, more preferably ranges from about 450°C to about 800°C, and most preferably ranges from about 550°C to about 700°C. The CF reactor 16 may be operated at atmospheric or slightly elevated pressures. The Gas Hourly Space Velocity (GHSV) preferably ranges from about 1,000 hr⁻¹ to about 100,000 hr⁻¹, more preferably from about 5,000 hr⁻¹ to about 50,000 hr⁻¹ and most preferably from about 10,000 hr⁻¹ to about 30,000 hr⁻¹. The Gas Hourly Space Velocity is defined as the volume of reactants per reaction zone volume per hour. The volume of reactant gases is determined at standard conditions of pressure (101 kPa) and temperature (0°C). In the case where CF reactor 16 is a fluidized bed reactor, the reaction zone

volume is defined as the total reaction zone volume, i.e., the expanded bed volume in a fluidized system which comprises less than 100% catalyst. On the other hand, if CF reactor 16 is a fixed bed reactor, the reaction zone volume is volume of the catalyst bed.

[0021] In addition, product stream 18, which contains the carbon filaments produced by CF reactor 16, is fed to a metal loading unit 22 to form metal on the carbon filaments. Metal loading unit 22 may include any known process for loading metal on the carbon filaments. The temperature of the metal loading process may be less than about 800°C, and is preferably less than about 400°C, to ensure that the carbon filaments do not become damaged by exposure to high temperatures. When the temperature of metal loading unit 22 is greater than 400°C, it is desirable to keep the molecular oxygen concentration in metal loading unit 22 preferably below 15 mole (mol) %, more preferably below 5 mol%, and most preferably below 1 mol%, to minimize carbon oxidation. When the temperature of metal loading unit 22 is lower than 400°C, then there is no need to maintain the molecular oxygen concentration below a certain value in metal loading unit 22. The type and the amount of metal loaded on the carbon filaments may vary depending on the end use application of the carbon filaments and would be obvious to one skilled in the art. Examples of suitable metals that may be formed on the carbon filaments include: precious metals such as platinum (Pt), palladium (Pd), ruthenium (Ru), and rhodium (Rh); other transition metals such iron (Fe), cobalt (Co), nickel (Ni), molybdenum (Mo), and copper (Cu); alkali metals such as lithium (Li); other metals such as silicon (Si); and combinations thereof. Preferably, the carbon filaments are loaded with at least about 1 weight (wt.) % metal per total weight of the carbon filaments.

[0022] An example of a suitable metal loading process is electroplating. To perform electroplating, carbon filaments may be suspended in an aqueous or organic solution containing a metal salt such as $\text{Cu}(\text{NO}_3)_2$, followed by placing the solution in a cell containing a suitable

cathode such as mercury (Hg). As the carbon filaments migrate to the cathode, they become charged such that they become part of the cathode. A voltage lower than the reduction potential of the metal is applied to the cathode to maintain a driving force such that the metal salt deposits on the carbon filaments and becomes reduced.

[0023] Alternatively, metal may be loaded on the surfaces of the carbon filaments by chemical vapor deposition (CVD). In CVD, carbon filaments are passed into a reaction chamber containing one or more volatile metallic compounds, e.g., organometallic compounds such as nickel carbonyl, tetra ethyl ortho silicate (TEOS), molybdenum oxide, methyl lithium, or butyl lithium. When the metal precursor is TEOS, silicon carbide nanofibers are formed on the carbon filaments. Carbon filaments are preferably less than about 1,000 nanometers (nm) in size, more preferably from about 5 to 500 nm, and most preferably from about 5 to 200 nm. The carbon filaments have an aspect ratio of length over diameter that is preferably greater than 5, more preferably in the range of from about 10 to about 2,000 nm. The filament aggregates (also called bundles) are preferably less than 1 millimeter in size. Carbon filaments are also called carbon fibrils or carbon nanotubes; they may be hollow or filled nanotubes and may contain a discontinuous or continuous carbon overcoat. As used herein, nanofibers refer to carbon filaments ranging from about 5 nm to about 500 nm in diameter, preferably from about 50 nm to about 200 nm in diameter.

[0024] The CVD reaction chamber is operated at any suitable conditions for decomposing and condensing the organometallic compounds, thereby forming metal radicals and/or ions that adsorb on the surfaces of the carbon filaments. The configuration and operation of CVD reactors are known in the art. The particular gas flowrate, reactor temperature, and reactor pressure (typically sub-atmospheric) employed can vary depending on, for example, the type of metal being deposited. Additional disclosure regarding the CVD process can be found in Campbell, Stephen

A. The Science and Engineering of Microelectronic Fabrication. New York: Oxford University Press, 2001, which is incorporated by reference herein in its entirety.

[0025] Yet another process that may be used to load metal on the surfaces of the carbon filaments is wet impregnation. A wet impregnation method that can be used to add metal to carbon filaments comprises the following steps: a) dissolving at least one metal precursor in a solvent to produce a metallic solution; b) depositing said metallic solution onto carbon filaments; c) optionally filtering the carbon filaments; d) drying the carbon filaments at a temperature in the range of from about 80°C to about 150°C; and e) heat-treating the dried carbon filaments at a temperature below about 800°C. The metal precursor preferably comprises a metal ion and a counter-ion, such as a hydroxide, a nitrate, an oxide, a chloride, or an organic moiety. The preferred metal precursor comprises Group VIII metals, more preferably Li, Pt, Pd, Ni, Cu, and Sn. The solvent is preferably water or an organic medium such as methanol, acetone, ethanol, or toluene. Depositing is preferably done by impregnation, such as incipient wetness impregnation. The heat treatment step e) is preferably performed in an inert atmosphere, such as an atmosphere comprising nitrogen and argon.

[0026] A product stream 24 recovered from metal loading unit 22 contains carbon filaments coated with metal. If desired, the carbon filaments may be passed back to CF reactor 16 (indicated by a dashed line 26) to repeat the carbon growth and metal loading processes. Multiple stages of metal loading and carbon growth can be repeated as many times as desired to form multiple layers of carbon and metal and to form branched carbon filaments. Since deposited metals are growth points leading to multidimensional carbon products of varying morphology, the number of stages and/or recycles may be selected based on the morphologies necessary for desired applications that require, for example, layered metal-carbon structures.

[0027] Fig. 2 depicts another embodiment like that shown in FIG. 1 except that a single CVD/CF reactor 30 is used instead of separate CF and CVD reactors. Alkanes from stream 14 and vaporized metallic compounds (combined with stream 14 or fed separately) are passed concurrently to CVD/CF reactor 30. As described previously, stream 14 may optionally contain small amounts of N₂ and H₂ in the aforementioned ratios. Within CVD/CF reactor 30, the metal is deposited on the carbon filaments as they are being formed such that the metal becomes incorporated within the carbon matrix of the filaments. Alternatively, a single compound, e.g., TEOS, may be fed to CVD/CF reactor 30 to form metal carbide nanofibers such as silicon carbide nanofibers.

[0028] The CVD/CF reactor 30 is configured to support both the CVD and carbon growth processes and to accommodate removal of metal filled carbon filaments from the reaction chamber via product stream 32. The reaction chamber may be operated at conditions appropriate for both the CVD process and the carbon growth process. In particular, it may be operated at a temperature in the range of from about 350°C to about 800°C, more preferably in the range of from about 450°C to about 750°C, and most preferably in the range of from about 550°C to about 700°C; and it may be operated at a pressure in the range of from about 0 atm to about 20 atm (about 0 to 2,000 kPa), more preferably in the range of from about 0 atm to about 10 atm (about 0 to 1,000 kPa), and most preferably in the range of from about 0 atm to about 5 atm (about 0 to 500 kPa). The GHSV preferably ranges from about 1,000 hr⁻¹ to about 100,000 hr⁻¹, more preferably from about 5,000 hr⁻¹ to about 50,000 hr⁻¹ and most preferably from about 10,000 hr⁻¹ to about 30,000 hr⁻¹. In addition to product stream 32, a stream 34 consisting essentially of H₂ may also exit CVD/CF reactor 30.

[0029] According to yet another embodiment shown in Fig. 3, alkenes formed via oxidative dehydrogenation (ODH), dehydrogenation, thermal cracking, or combinations thereof may be

converted to carbon filaments, followed by loading the carbon filaments with metal. A description of a suitable integrated ODH/CF process can be found in copending U.S. Patent Application Serial No. 10/288,710, filed November 05, 2002 and entitled "INTEGRATED OXIDATIVE DEHYDROGENATION / CARBON FILAMENT PRODUCTION PROCESS AND REACTOR THEREFOR," which is incorporated by reference herein in its entirety. In addition, dehydrogenation and thermal cracking of hydrocarbons are well known in the art. A suitable thermal cracking process is disclosed in U.S. Patent No. 5,925,799, which is incorporated by reference herein in its entirety. A suitable dehydrogenation process is the OleflexTM process of UOP LLC of Des Plaines, Illinois, as described in OleflexTM Process for Propylene Production. 1998. <http://www.uop.com/techsheets/oleflex.pdf>, which is incorporated by reference herein in its entirety.

[0030] Referring to Fig. 3, a feed stream 40 comprising hydrocarbons and a feed stream 42 comprising molecular oxygen (O₂) are fed to an alkene synthesis reactor (ASR) 44 to produce alkenes from the hydrocarbons. Alternatively, hydrocarbons and oxygen may be combined into a single feed stream. Feed stream 40 may contain any gaseous hydrocarbons such as natural gas, associated gas, light hydrocarbons having from 1 to 10 carbon atoms, or naphtha. Preferably, feed stream 40 comprises at least 50% by volume light alkanes (e.g., methane, ethane, and propane), which may be recovered from a gas plant for processing natural gas into different fractions. Feed stream 42 may contain, for example, pure oxygen, air, oxygen-enriched air, or oxygen mixed with a diluent.

[0031] In preferred embodiments, ASR reactor 44 comprises a catalyst, and at least a portion of the hydrocarbons undergo catalytic dehydrogenation in the presence of the catalyst to produce an effluent stream comprising CO, CO₂, H₂, H₂O, alkenes, and unconverted hydrocarbons. Preferably, the catalyst is active in the ODH reaction of light hydrocarbons.

A separator (not shown) may be employed to separate the product gas from the ASR reactor 44 into an alkene stream 46 comprising substantially or alternatively consisting essentially of alkenes for feeding to a CF reactor 50 and a synthesis gas stream 48 comprising substantially or alternatively consisting essentially of H₂ and CO for feeding to another downstream process. Hydrocarbon conversion within the ASR reactor 44 typically is less than 100 percent in a single pass, and thus the unconverted hydrocarbons may optionally be separated and recycled back to feed stream 40 (not shown). Alternatively, the unconverted hydrocarbons may be fed to CF reactor 50.

[0032] Any suitable reactor configuration may be employed to convert the reactants in the ASR reactor 44. When ASR reactor 44 comprises a dehydrogenation catalyst, one suitable configuration is a fixed catalyst bed in which the catalyst is retained within a reaction zone in a fixed arrangement. Dehydrogenation catalysts may be employed in the fixed bed regime using fixed bed reaction techniques known in the art.

[0033] In preferred embodiments, ASR reactor 44 contains an ODH catalyst and is a short-contact time reactor, e.g., a millisecond contact time reactor of the type used in synthesis gas production. A general description of major considerations involved in operating a reactor using millisecond contact times is given in U.S. Patent No. 5,654,491, which is incorporated herein by reference. Additional disclosure regarding suitable ASR reactors comprising an ODH catalyst and the ODH process is provided in commonly owned published US Patent Application No. 20030040655 A1 (Serial No. 10/106,709), entitled "Oxidative dehydrogenation of alkanes to olefins using an oxide surface," Schmidt et al, New Ways to Make Old Chemicals, Vol. 46, No. 8 AIChE Journal p.1492-95 (August 2000); Bodke et al, Oxidative Dehydrogenation of Ethane at Millisecond Contact Times: Effect of H₂ Addition, 191 Journal of Catalysis p. 62-74 (2000); Iordanoglou et al, Oxygenates and Olefins from Alkanes in a Single-Gauze Reactor at Short

Contact Times, 187 Journal of Catalysis p. 400-409 (1999); and Huff et al, Production of Olefins by Oxidative Dehydrogenation of Propane and Butane over Monoliths at Short Contact Times, 149 Journal of Catalysis p. 127-141 (1994), each of which is incorporated by reference herein in its entirety.

[0034] In embodiments in which the ASR reactor 44 comprises an ODH catalyst, the hydrocarbon feedstock and the oxygen-containing gas are contacted with the ODH catalyst in a reaction zone that is maintained at conversion-promoting conditions effective to produce alkenes. Feed streams 40 and 42 are preferably pre-heated before contact with the ODH catalyst. The process is operated at atmospheric or super atmospheric pressures, the latter being preferred. The pressure may range from about 100 kPa to about 12,500 kPa, preferably from about 130 kPa to about 5,000 kPa. The catalyst temperature may range from about 400°C to about 1200°C, preferably from about 500°C to about 900°C. The gas hourly space velocity (GHSV) for the process, stated as normal liters of gas per kilogram of catalyst per hour, ranges from about 20,000 hr⁻¹ to at least about 100,000,000 hr⁻¹, preferably from about 50,000 hr⁻¹ to about 50,000,000 hr⁻¹. Residence time is inversely proportional to space velocity, and high space velocity indicates low residence time on the catalyst. In a preferred millisecond contact time reactor, the residence time of the reactant gas mixture with the ODH catalyst is no more than about 100 milliseconds.

[0035] ODH catalysts may be of any suitable composition and form, including foam, monolith, gauze, noodles, spheres, pills or the like, for operation at the desired gas velocities with minimal back pressure. Typically, ODH catalysts contain a precious metal such as platinum to promote the conversion of hydrocarbons to alkenes. For example, U.S. Patent No. 6,072,097 and WO Pub. No. 00/43336 describe the use of platinum and chromium oxide-based monolith ODH catalysts for ethylene production with SCTR; U.S. Patent No. 6,072,097 describes the use of Pt-coated monolith ODH catalysts for use in SCTR; and WO Patent No. 00/43336 describes the use of Cr,

Cu, Mn or this mixed oxide-loaded monolith as the primary ODH catalysts promoted with less than 0.1% Pt, each of these references being incorporated herein in their entirety. Alternative ODH catalysts are available that do not contain any unoxidized metals and that are activated by higher preheat temperatures. Examples of preferred alternative ODH catalysts that do not contain any unoxidized metal are disclosed in copending U.S. Pat. Applications 60/309,427, filed August 1, 2001 and entitled "Oxidative Dehydrogenation of Alkanes to Olefins Using an Oxide Surface" and 60/324,346, filed September 24, 2001 and entitled "Oxidative Dehydrogenation of Alkanes to Olefins Using Non-Precious Metal Catalyst", which are incorporated by reference herein in their entirety.

[0036] Referring again to Fig. 3, alkene stream 46 is passed to CF reactor 50 to produce carbon filaments. As mentioned previously, unconverted hydrocarbons from ASR reactor 44 may also be passed to CF reactor 50. The growth and recovery of the carbon filaments is performed in the same manner as described in reference to Fig. 1 with the exception that primarily alkenes rather than alkanes are disassociated to form the carbon filaments. A H₂ stream 54 and a carbon filament stream 52 exit the CF process. The carbon filaments from stream 52 are then subjected to a metal loading process 56 to form metal thereon. Any of the previously described metal loading processes, such as CVD, electroplating, or wet impregnation, may be employed. As a result, carbon filaments coated with metal are recovered from metal loading process 56 via stream 58. Optionally, as indicated by dashed line 60, the metal coated carbon filaments can be recycled back to CF reactor 50 and metal loading process 56 any many times as desired to form multiple layers of carbon filaments and metal.

[0037] Fig. 4 depicts yet another embodiment like that shown in Fig. 3 except that a single CVD/CF reactor 64 is used instead of separate CF and CVD reactors. Alkenes from ASR reactor 44 and vaporized metallic compounds are concurrently passed to CVD/CF reactor 64. As a result,

metal is deposited on the carbon filaments as they are being formed such that the metal becomes incorporated within the carbon matrix of the filaments. The CVD/CF reactor 64 may be operated in the same manner as CVD/CF reactor 30 of Fig. 2. Carbon filaments filled with metal may be recovered from CVD/CF reactor 64 via stream 66, and H₂ may be recovered from CVD/CF reactor 63 via stream 68.

[0038] The metal loaded carbon filaments formed in the processes shown in Figs. 1-4 exhibit excellent properties such as increased electrical conductivity and enhanced H₂ storage. For example, they typically have resistivities in the range of from about 10⁻⁴ to about 10⁴ ohms/cm², and they can typically store from about 0.1 –to about 10 wt. % H₂ per total weight of the carbon filaments. As such, they can be used to form improved end use articles such as electronic elements (e.g., transistors, sensors, and wires), composite materials having enhanced electrical properties, and metal catalysts (e.g., Fischer-Tropsch catalysts, ODH catalysts, and alcohol producing catalysts) having high surface area carbon support structures. Those skilled in the art would know how to make and use such end use articles. Further, the present invention contemplates forming high strength materials such as metal carbide nanofibers.

EXAMPLES

[0039] The invention having been generally described, the following example is given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

[0040] Carbon filaments were prepared using a tube furnace with a quartz reactor tube containing a Monel screen (1"W x 6"L). First, the tube furnace was heated to 650°C under N₂ flow at 200 mL/min. Once the temperature reached 650°C, ethylene flowing at 200 mL/min and N₂ flowing at 60 mL/min were fed to the furnace, and the exit gases were analyzed using a gas

chromatograph (GC) containing a thermal conductivity detector (TCD) for hydrocarbon products. The reaction was continued at 650°C for a time period ranging from 1 hour to 4 hours, with 2 hours being the standard run length. After this time, the gas flows were stopped, and the reactor was allowed to cool down to room temperature. Then the reactor was opened, and the carbon sample was brushed off from the Monel screen inside a glove box to prevent carbon fines from affecting the lab atmosphere. On an average, about 5-10 grams of carbon were made per hour at these run conditions.

[0041] The following impregnation method was employed to deposit Li on carbon filaments:

(a) the carbon filaments were sieved using a 14-mesh screen to separate the coarse filaments from the fines; (b) the coarse sample was washed with distilled and de-ionized (DDI) water and then with acetone and dried at 100°C overnight to remove the volatiles; (c) the dried coarse sample was sonicated in an ultrasonic bath for 20 minutes using TRITON X-100 surfactant (commercially available from E.I. DuPont de Nemours and Company) diluted with water at a volume ratio of 1:100, allowed to stand for 1 hour, and filtered by applying vacuum; and (d) the residue on the filter paper was dried in a convection oven using air at about 100°C overnight. Steps (a) – (d) were performed to clean the sample and collect higher purity carbon filament bundles. Figure 5 depicts a SEM picture of the pretreated carbon filament sample before metal modification.

[0042] Next, an ALDRICH 25,427-4 aqueous solution containing lithium hydroxide in DDI water (available from Aldrich Chemical Co.) was added to the pretreated carbon filament sample such that the sample contained 5 wt.% Li based on the weight of the carbon. The sample was then stirred while heating at 70 to 80°C on the hotplate for 3 hours and dried in a convection oven in air at about 100°C overnight, followed by calcination in air at 250°C for 3 hours. The resulting sample after calcination contained a coating of lithium oxide on carbon and is shown in the SEM picture in Fig. 6.

[0043] Based on the SEM image shown in Fig. 6, the impregnation method did not result in uniform coating of Li on the carbon. Most of the carbon filaments were covered with lithium oxide (a bright colored coat). Some of the filaments also showed incorporation of the metal oxide inside the filaments since the hollow portions appeared to be covered.

[0044] The following table shows the BET surface areas of carbon filament samples prepared as a function of reaction temperature and feed composition using Monel catalyst screens, wherein BET surface area measurements are well known in the art. These samples were not coated with any metal compounds. This table is intended only to show the variation that can be achieved in the filament properties by controlling the process parameters and is not meant to limit the scope of the invention. Any of these filaments could be coated with metal/metal oxide/metal compounds as desired to achieve the required surface areas.

Table-1: BET surface areas of carbon filaments (before metal deposition)

Feed composition (wt.%), Catalyst	Reaction temperature (°C)	BET surface area of the resulting carbon filaments (m ² /g)
100 % ethylene, Monel screen	500	114
100% ethylene, Monel screen	650	345
100% ethylene, Monel screen	800	221
100% ethylene, Ni screen	750	137

[0045] While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any

element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claims.

[0046] Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the preferred embodiments of the present invention. The discussion of a reference in the Description of Related Art is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.